

Effect of Zone Drawing on the Structure and Properties of Melt-Spun Poly(trimethylene terephthalate) Fiber

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ABSTRACT: Melt-spun poly(trimethylene terephthalate) (PTT) fibers were zone-drawn and the structures and properties of the fibers were investigated in consideration of the spinning and zone-drawing conditions. The draw ratio increased up to 4 with increasing drawing temperature to 180°C, at a maximum drawing stress of 220 MPa. Higher take-up velocity gave lower drawability of the fiber. The PTT fiber taken up at 4000 rpm was hardly drawn, in spite of using maximum drawing stress, because a high degree of orientation had been achieved in the spinning procedure. However, an additional enhancement of birefringence was observed, indicating a further orientation of PTT molecules by zone drawing. The exotherm peak at 60°C disappeared and was shifted to a lower temperature with an increase in the take-up velocity, which means that the orientation and crystallinity of the fiber increased. The *d*-spacing of (002) plane increased with increasing take-up velocity and draw ratio, whereas those of (010) and (001) planes decreased. In all cases, the crystal size increased with take-up velocity and draw ratio. The cold-drawn PTT fiber revealed a kink band structure, which disappeared as the drawing temperature was raised. The physical properties of zone-drawn PTT fibers were improved as the draw ratio and take-up velocity increased. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 3471–3480, 2001

Key words: PTT fiber; zone drawing; draw ratio; take-up velocity

INTRODUCTION

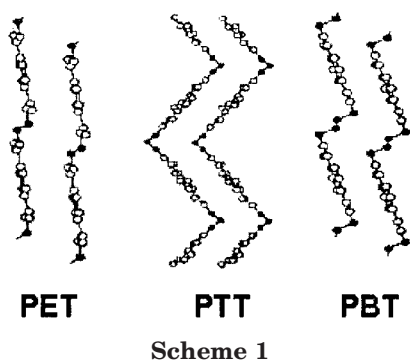
Although the mechanical properties of poly(ethylene terephthalate) (PET) are good enough to warrant its use as fibers, films, and engineering plastics, there are some difficulties in processing PET because of its high melting temperature. Several researchers have concentrated on the enhance-

ment of the processibility of PET with superior mechanical properties.^{1–6} The diacid group affects the mechanical property of polyester and, in addition, its processibility depends on the type of the diol group. In particular, poly(trimethylene terephthalate) (PTT), synthesized using 1,3-propanediol as a diol, is a high crystalline polymer. Its melting temperature is lower than that of PET by 20–30°C. Therefore, the processibility of PTT is superior to that of PET. Furthermore, the highly flexible PTT fibers are obtained as a result of its low initial modulus. The elasticity and dyeability of PTT are better than those of PET or poly(butylene terephthalate) (PBT), which makes it possible to use PTT as engineering plastics, films, car-

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pets, and clothing materials. For these reasons, PTT is considered as the most promising candidate for a replacement of PET.

It is well known that the number of methylene unit influences the physical properties of many polycondensation polymers such as polyamide and polyester, which is called the odd-even effect. As shown in **Scheme 1**, PET molecules are fully extended with two carboxyl groups of each terephthaloyl group in opposite directions, and all open-chained bonds are *trans* with successive phenylene groups at the same inclination along the chain.⁶ PTT has a conformation with bonds of the $-\text{O}-(\text{CH}_2)_3-\text{O}-$ unit having the sequence of *trans-gauche-gauche-trans*, leading to a concentration of the repeating unit. The opposite inclinations of successive phenylene groups along the chain force the molecular chains to take on an extended zigzag shape.

Because of the molecular characteristic differences already described, the theoretical maximum elongations (*c*-axis that is parallel to the fiber axis) of PET and PBT reach about 98 and 86%, respectively, whereas that of PTT is only 76%. The crystal lengths in the fiber axis of PET and PBT coincide with those of fully extended lengths [PET, 98%; PBT, 88% (α -type), 96% (β -type)]. On the contrary, PTT has a helical structure of an angle of 60° (*gauche*) for its odd-numbered carbons, resulting in the 75% gain of fully extended chain length. For this reason, to enhance the physical properties of PTT fibrous materials, the PTT chain should be extended with the change in distortion angles in crystalline as the spring extension.⁷

The zone-drawing or zone-annealing method is one of the techniques that yield high-modulus and high-strength fibers. The zone-drawing technique shows many advantages compared to hot-drawing experiments, such as reduced probabilities of microcrystallite formation, back folding of molecular

chains, and thermal degradation of the sample. The zone-drawing method has already been applied to many polymeric fibers and films, including PET,^{8,9} in our investigations.⁸⁻²⁰ However, it has rarely been adopted for PTT fiber having a similarity in chemical structure and a difference in molecular conformation. In this study, zone drawing was conducted for the effective orientation of the molecular chain of PTT. The effects of zone-drawing conditions on the structure and physical properties of melt-spun PTT fibers were investigated.

EXPERIMENTAL

Materials

The PTT chips (intrinsic viscosity of 0.92 dL/g) used in this study were kindly supplied by Shell Chemical Company. Prior to spinning, each PTT chip was dried in a vacuum oven at 140°C for 24 h. Other ultrapure-grade reagents were used without further purification.

Melt Spinning of PTT

PTT fibers were produced by melt spinning at take-up velocities of 1000, 2000, 3000, and 4000 rpm and spinning temperatures of 235, 245, 255, and 265°C , respectively.

Zone Drawing of PTT Fiber⁸⁻²⁰

Zone drawing was carried out at several temperatures by moving a pair of narrow-band heaters [$7\text{ cm} \times 2.5\text{ cm} \times 1\text{ mm}$ (length \times width \times thickness)] along the film. A PTT fiber of 10 cm length was drawn under tensions controlled by different dead weights on an Instron model 4201. The zone-drawing conditions are listed in Table I.

Characterization

Birefringences, measured on an Olympus BH-2 polarizing microscope (Olympus Corp., Lake Success, NY) with senarmont compensator, were de-

Table I Zone-Drawing Conditions of PTT Fiber

Drawing stress (MPa)	30, 50, 75, 90, 120, 150, 175, 200, 220
Drawing temperature ($^\circ\text{C}$)	130, 150, 180
Heat band speed (mm/min)	10

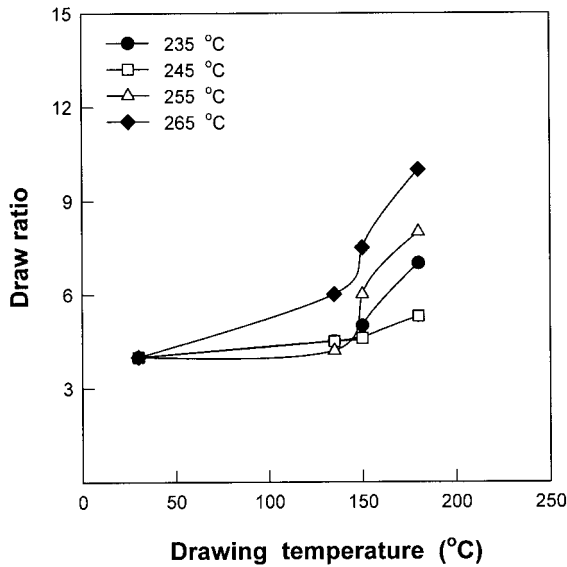


Figure 1 Draw ratios of PTT fibers at different spinning temperatures with drawing temperatures.

terminated by dividing the optical path length by the thickness.

Differential scanning calorimetry (DSC) measurements were carried out using a DSC 2010 (TA Instruments, New Castle, DE). The DSC scans were performed within the temperature range of 10–250 °C, using a heating rate of 10 °C/min. All measurements were carried out under nitrogen purge.

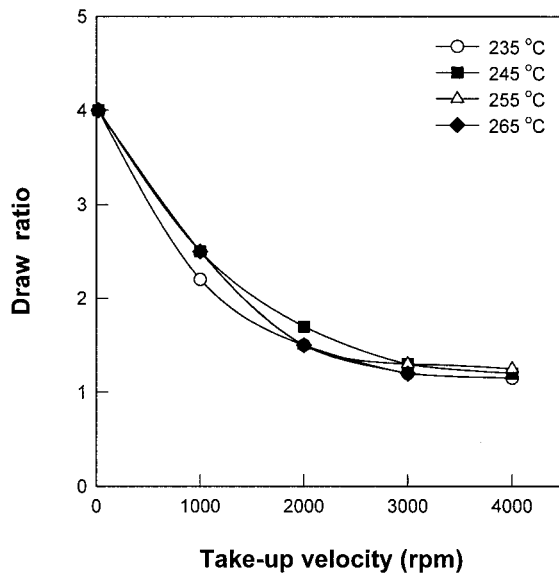


Figure 2 Draw ratios of PTT fibers zone-drawn at 180 °C at different spinning temperatures with take-up velocities.

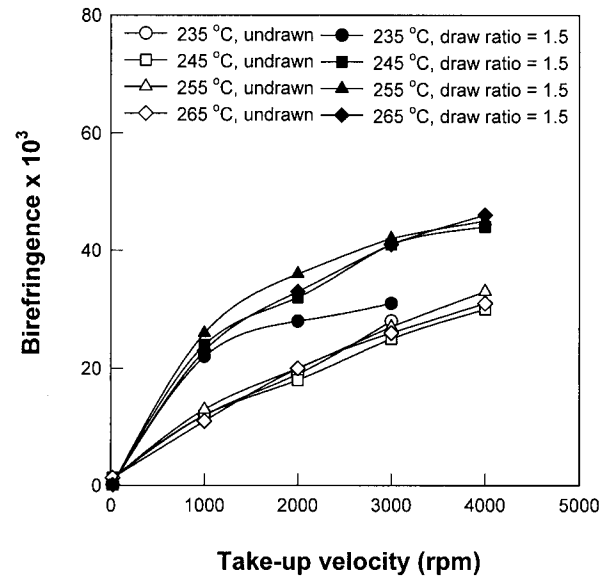


Figure 3 Birefringences of undrawn and drawn PTT fibers at different spinning temperatures with take-up velocities.

Wide-angle X-ray diffraction data of PTT fibers were obtained using an X-ray diffractometer (D/Max-2500; Rigaku, Japan) with nickel-filtered $\text{CuK}\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$) at 40 kV and 30 mA. Crystalline parameters, such as lattice spacing (d) and crystalline size (D), were calculated from eqs. (1) and (2), respectively:

$$d = (K\lambda)/(2 \sin \theta) \quad (1)$$

$$D = (K\lambda)/(\beta \cos \theta) \quad (2)$$

where $K = 0.94$ and β is the full width at half maximum of the peak at θ .

Surface morphology of PTT fibers was examined by Hitachi S4100 microscope and Nikon Optiphot-Pol 104 polarized optical microscope.

The tensile properties were determined with a Testometric MICRO 350 Instron. Tensile modulus, tensile strength, and elongation at break were calculated from the stress–strain curves obtained at 25 °C and 65% relative humidity.

RESULTS AND DISCUSSION

Results of this investigation pertaining to the improvement of mechanical properties and the structural and morphological changes of PTT fibers induced by the spinning condition and zone

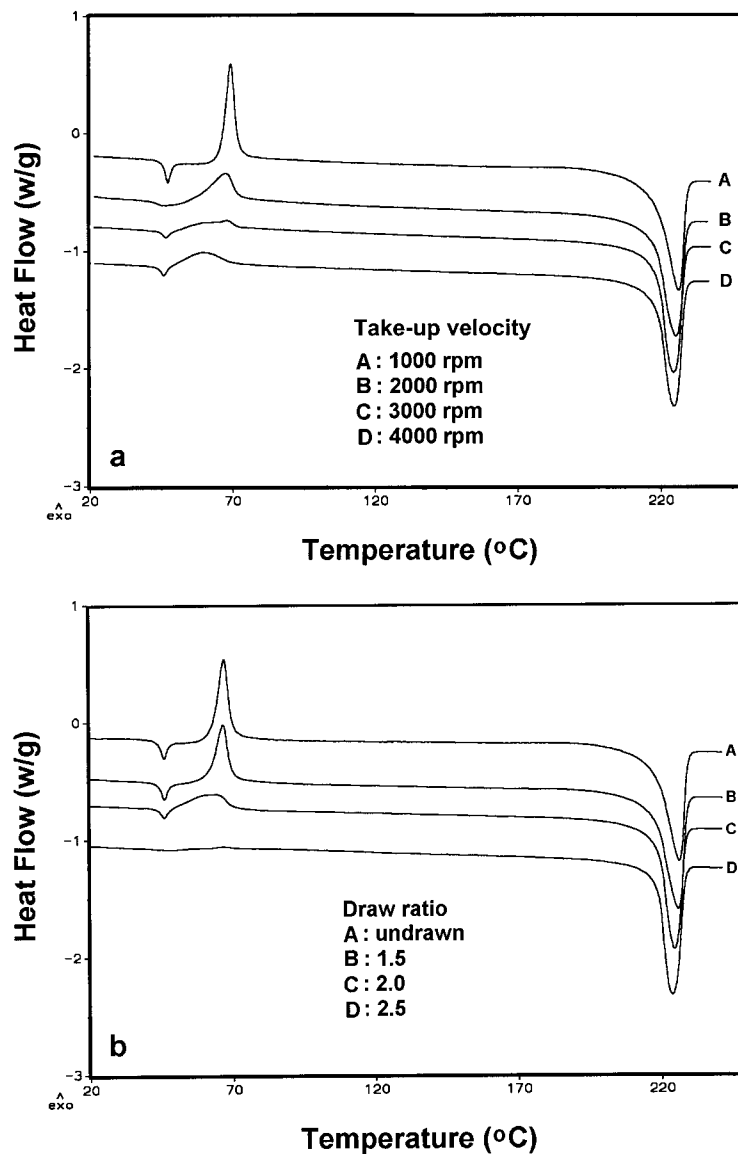


Figure 4 DSC curves for PTT fibers produced at different take-up velocities (a) and at different draw ratios (b), using spinning temperature of 255°C.

drawing are presented. The effect of zone-drawing conditions on the structure and properties was investigated by varying drawing temperatures and drawing stresses. The condition attaining the maximum draw ratio was chosen as the one for further zone-drawing treatment. The maximum drawing stress of 220 MPa was used. Under a higher drawing stress of 220 MPa, a breakage of fiber occurred.

Figure 1 shows the changes in draw ratios of PTT fibers spun at different temperatures with drawing temperature at a drawing stress of 220 MPa. Drawing was made from 30 to 180°C, respectively, and the drawing temperature of 180°C

was found to be maximum. The draw ratio increased with increasing drawing temperature below 180°C. Above 180°C, drawing was not conducted properly because the fiber tended to melt near the melting temperature. The draw ratio increased stiffly above 150°C, which may result from the fact that at a drawing temperature lower than 150°C, extension of the amorphous region was predominant, whereas those of the crystalline and amorphous regions took place simultaneously at a drawing temperature of 150–180°C.

Draw ratios of PTT fibers (drawing temperature of 180°C) spun at different temperatures with take-up velocity at a drawing stress of 220

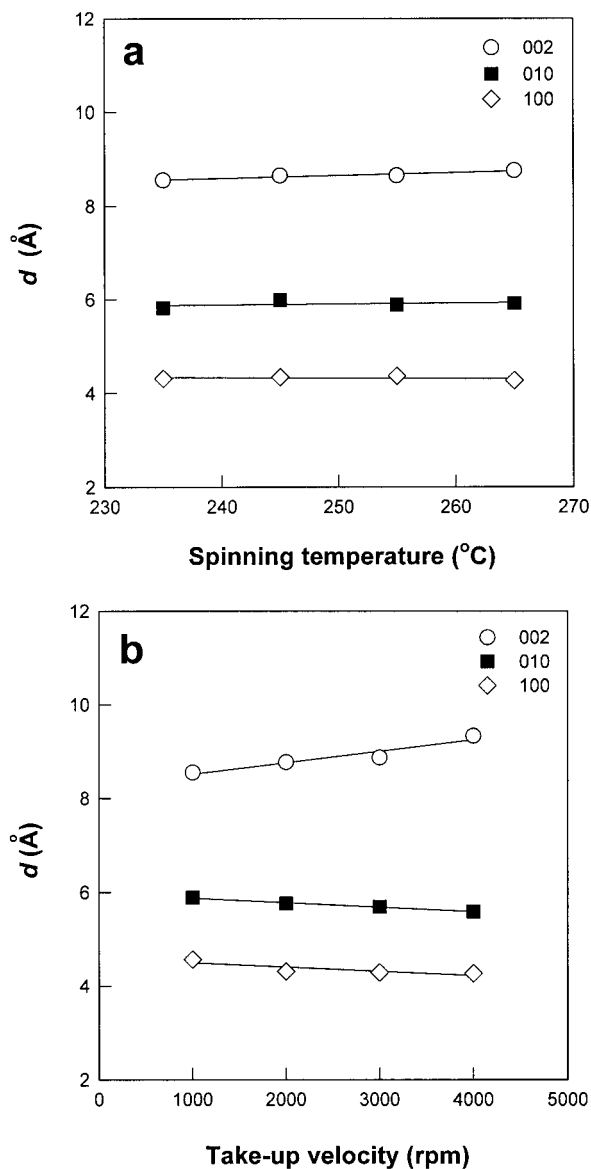


Figure 5 Effect of spinning temperature (a) and take-up velocity (b) on the d of the PTT fiber.

MPa are presented in Figure 2. As take-up velocity increased, draw ratios decreased. PTT molecules are quite highly oriented during high-speed spinning.²¹ During high-speed spinning of PTT, a substantial part of the orientation and crystallization takes place, although subsequent drawing procedures are necessary to produce further orientation and crystallization. In particular, the samples obtained at the take-up velocity of 4000 rpm were hard to be extended by zone drawing because the orientation and formation of crystal had been abundantly attained during the higher take-up process.

To examine the development of orientation during the spinning and drawing processes, the birefringence of PTT fiber was measured. Figure 3 shows the birefringences of PTT fibers at different take-up velocities and different spinning temperatures. The birefringence increased almost linearly with increasing take-up velocity up to 4000 rpm, indicating that the total degree of molecular orientation in both crystalline and amorphous regions increased for the samples produced at high take-up velocity. Moreover, as the draw ratio increased, the molecules had less time to relax as they crystallize, and so the degree of

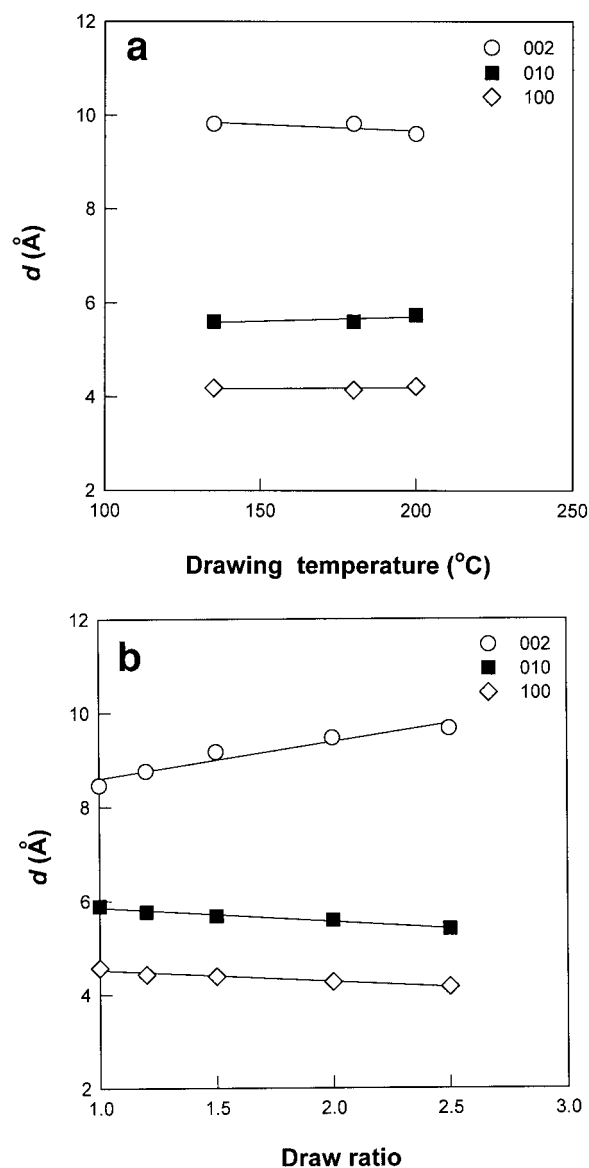


Figure 6 Effect of drawing temperature (a) and draw ratio (b) on the d of the PTT fiber.

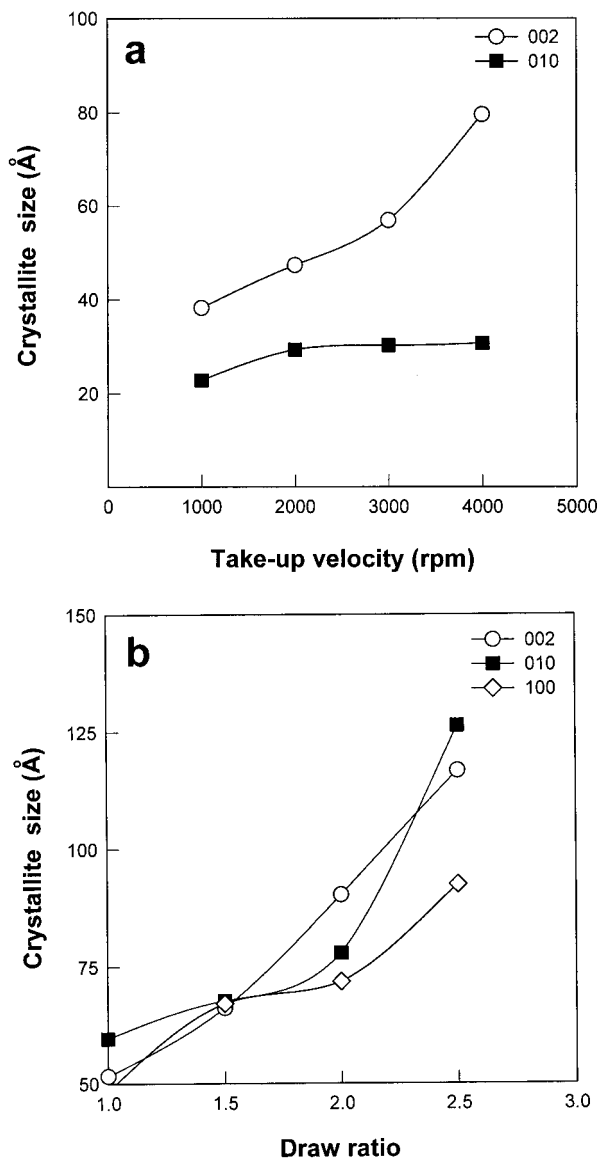


Figure 7 Dependence of the D of the PTT fiber on the take-up velocity (a) and draw ratio (b).

orientation increased. It is notable that with increasing take-up velocity up to 4000 rpm, the increase in birefringence of the drawn specimen was more pronounced, suggesting that the further orientation of PTT molecules was achieved by zone drawing, even at high take-up velocity.

DSC thermograms of PTT fibers produced at different take-up velocities and draw ratios are shown in Figure 4(a) and (b), respectively. It is observed that the crystallization peak at 60°C moved to low temperature and then disappeared as take-up velocity and draw ratio increased, suggesting that the crystallization took place along

with the orientation in the course of the spinning at high take-up velocity and the drawing with high draw ratio.

The influences of spinning conditions like spinning temperature and take-up velocity on the lattice spacing (d) of the PTT fiber, which was estimated from the (010) peak at $2\theta = 15.65^\circ$ in equatorial, the (100) peak at $2\theta = 20.35^\circ$ in equatorial, and the (002) peak at $2\theta = 10.15^\circ$ in meridional, respectively, are depicted in Figure 5. The spinning temperature had little effect on the value of d . In contrast, the d -value of the (002) plane increased with take-up velocity, whereas the d -value of (010) and (001) planes decreased, which implies the molecular orientation along the fiber axis was enhanced by the increase of take-up velocity. Figure 6 shows the effects of drawing conditions like drawing temperatures and draw ratios on d . The d -values were nearly constant with drawing temperature at the same drawing stress of 220 MPa. The d -value of the (002) plane increased with increasing draw ratio. On the contrary, the d -values of the (100) and (010) planes diminished with an increase in draw ratio. These show a similar trend with the results in Figure 5. However, it is noteworthy that the d of the (002)

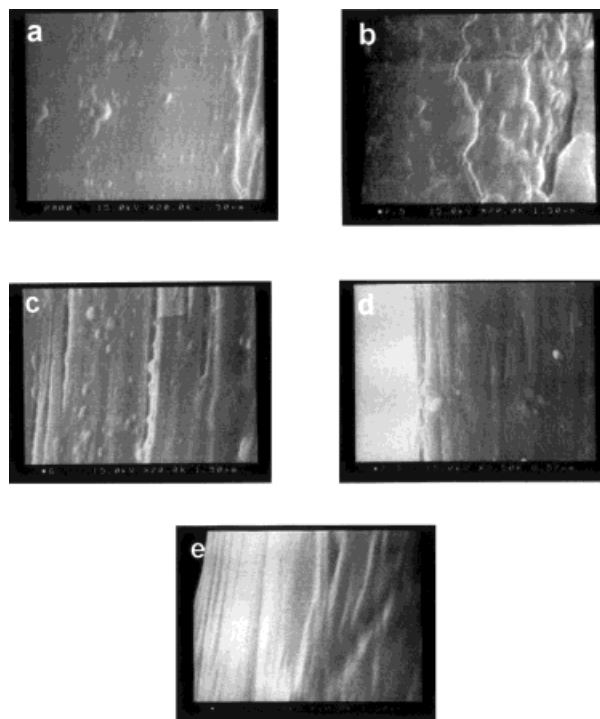


Figure 8 Effect of draw ratio on the surface morphology of PTT fiber. Draw ratio: (a) 1; (b) 3; (c) 6; (d) 8; (e) 10.

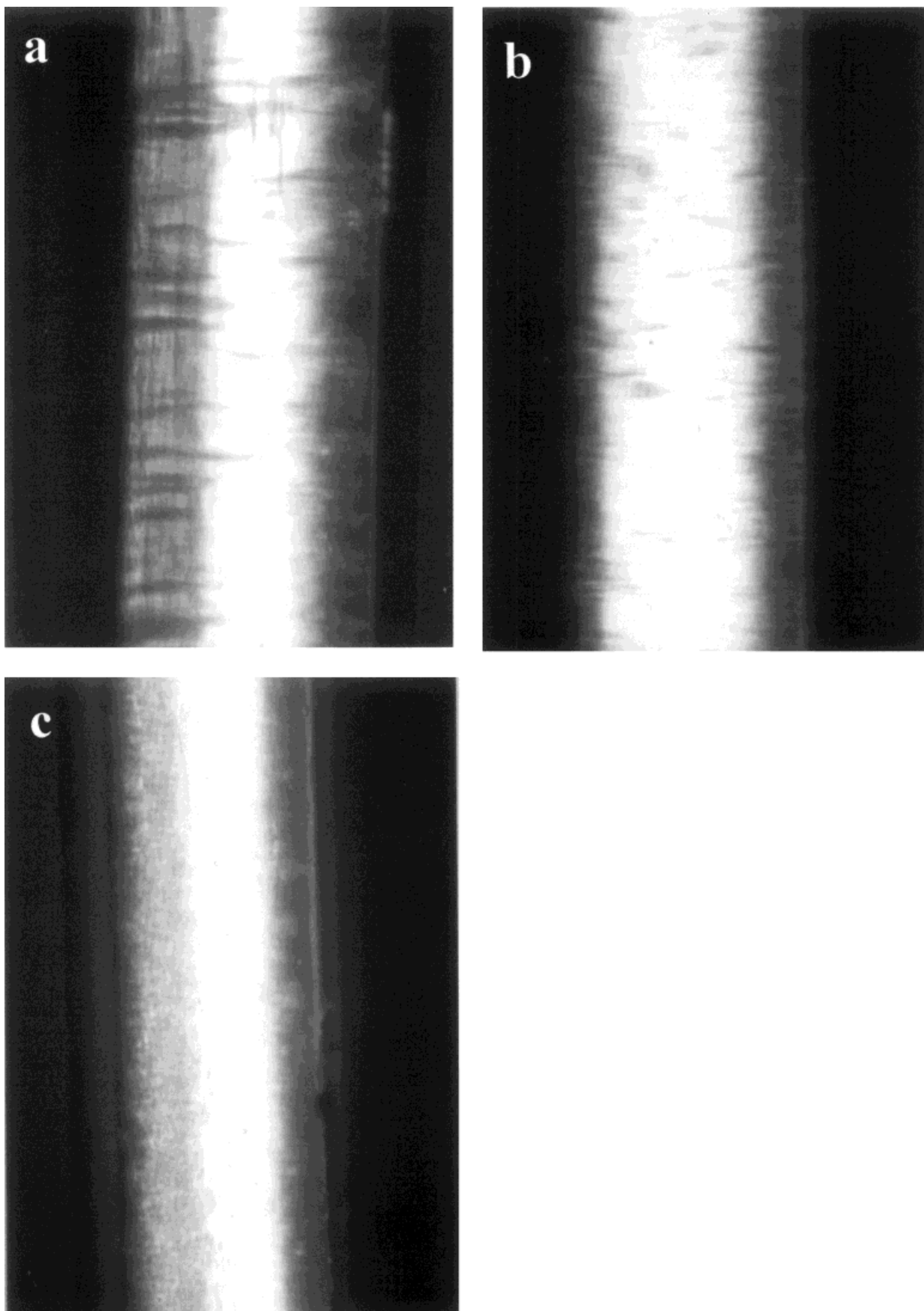


Figure 9 Morphologies of PTT fibers cold-drawn at 30°C (a), zone-drawn at 135°C (b), and zone-drawn at 180°C (c).

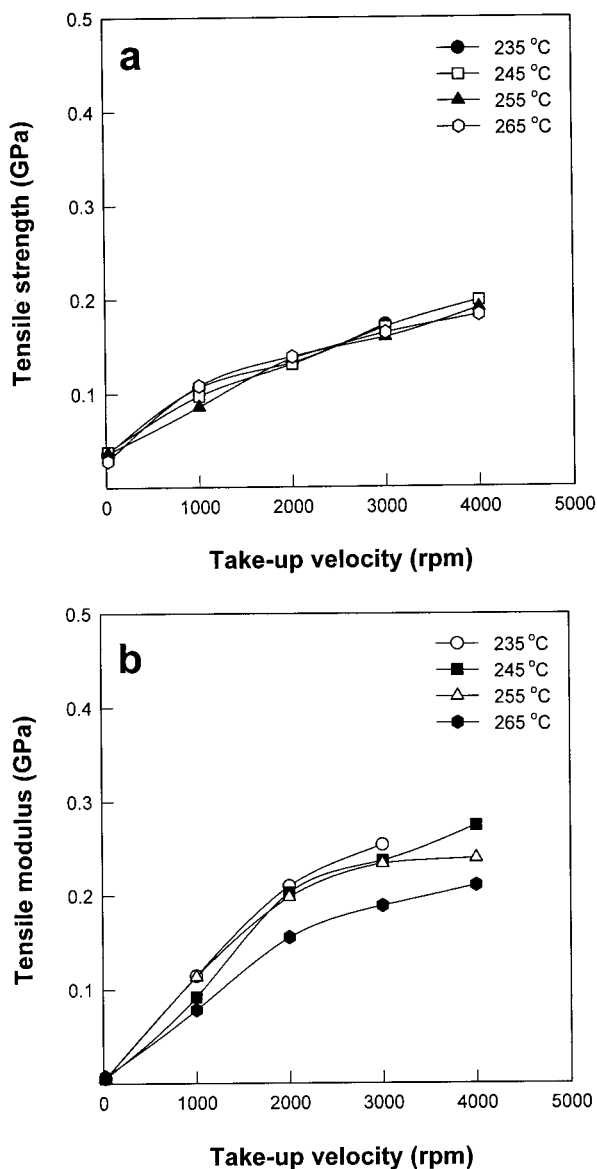


Figure 10 Tensile strength (a) and tensile modulus (b) of the undrawn PTT fiber at different spinning temperatures with take-up velocity.

plane of PTT was affected more strongly by draw ratio than by take-up velocity, which supports the result in Figure 3. The dependencies of crystal sizes (D) estimated from the full width at half maximum of (002), (010), and (001) reflections of the PTT fibers on the take-up velocity and draw ratio are presented in Figure 7. The increase in take-up velocity and draw ratio resulted in the increased D values of the (002), (010), and (100) planes.

Figure 8 shows scanning electron micrographs of the PTT fiber with various draw ratios. The

specimens were drawn at the same temperature of 180 °C, to precisely identify the draw ratio effect only. The fibrous structure preferentially oriented along the draw direction was developed with increasing draw ratio. The effect of drawing temperature on the morphology of PTT fiber was also investigated using a polarizing microscope. In Figure 9, the polarizing micrographs of PTT fibers cold-drawn at 30 °C [Fig. 9(a)] and zone-drawn at 135 °C [Fig. 9(b)] and 180 °C [Fig. 9(c)], respectively, were exhibited. The three PTT fibers are being drawn at the same drawing stress of 220

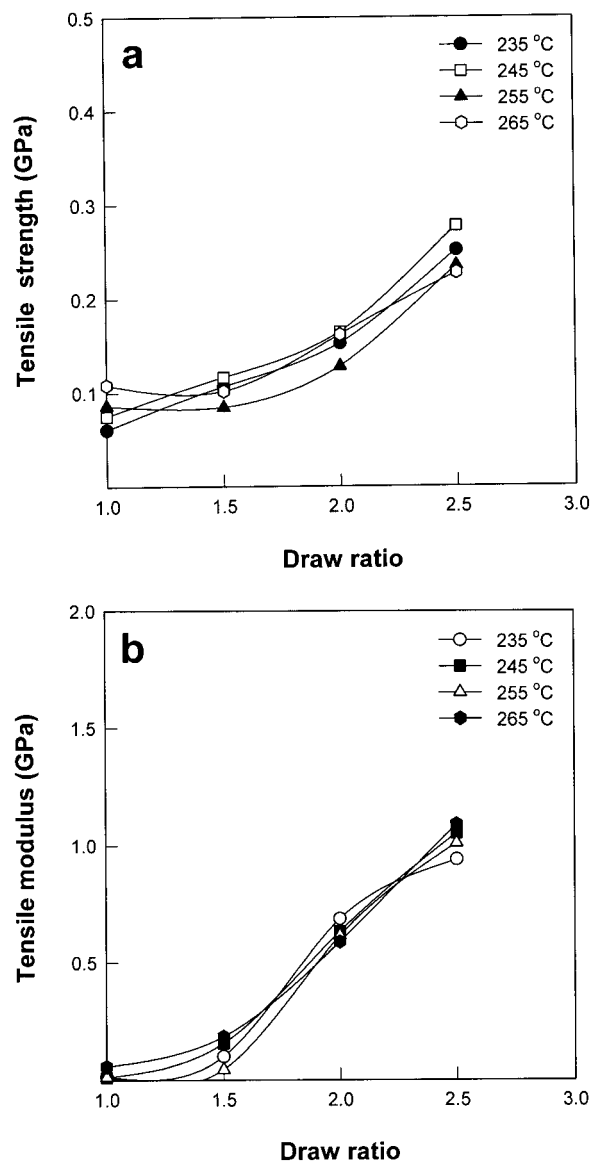


Figure 11 Tensile strength (a) and tensile modulus (b) of the PTT fiber produced using take-up velocity of 1000 rpm at different spinning temperatures with draw ratio.

MPa to clarify/identify the effect of drawing temperature only. The kink band structure was observed only in the cold-drawn specimen. The kink bands were first described in metals and salt crystals and have been observed in semicrystalline and amorphous-oriented polymeric samples as well.²² It is generally believed that the kink band formation is closely related to the fibrillar morphology of a fiber. However, it is unclear how a band develops and eventually leads to a complicated compressive failure.²³ For example, the formation of kink bands indicates the presence of a preferential slip plane parallel to the lamellar microdomains in the PTT fiber. Furthermore, kink band formation suggests that the microphase-separated domains remain intact and rotate during mechanical deformation.^{24–27} The mere existence of kink bands implies the presence of a preferential slip plane parallel to the lamella, which we estimated to exist within the PTT fiber microdomains. In cold drawing, the kink band structure was easily developed, as shown in Figure 9(a), because the PTT chain is extended only with difficulty. On the contrary, in the zone-drawing process, the chain extension is facilitated to disclose the smooth surface structure without the slip of plane, as shown in Figure 9(b).

The tensile strength and tensile modulus of PTT fiber with take-up velocity and draw ratio at different spinning temperatures are shown in Figures 10 and 11. With increases of take-up velocity and draw ratio, both tensile strength and tensile modulus increased. The strength and modulus of the fiber obtained at take-up velocity of over 2000 rpm increased slightly, whereas those obtained above a draw ratio of 1.5 rose stiffly. Hence, the enhancement of strength and modulus was achieved more effectively by increasing draw ratio than by increasing take-up velocity. For most series, elongation decreased with increasing take-up velocity, indicating that molecular orientation was favored when as-spun fibers were wound at higher speed, which is coincident with the result from Figures 2 and 3. However, because the PTT fiber in this study was prepared by melt spinning, relatively lower tensile strength and modulus than that produced by solution spinning (which is possible to introduce optimum polymeric tie molecules) were obtained.

CONCLUSIONS

By considering the effect of zone drawing on the structure and properties of melt-spun PTT fibers,

we are able to draw the following conclusions. Fine PTT fibers were produced by melt spinning at a high temperature of 235–265°C and subsequent zone drawing. The draw ratio increased stiffly above 150°C and maximum draw ratio of 4 was obtained at a drawing temperature of 180°C and at drawing stress of 220 MPa. Furthermore, the subsequent drawing of the fiber taken at 4000 rpm was hardly made, indicating that a high degree of orientation was achieved. The birefringence of the zone-drawn sample was higher than that of the undrawn, implying that further orientation of PTT molecules was available by zone drawing. An exotherm peak at about 60°C disappeared as take-up velocity increased, which means that the orientation and crystallinity of fiber increased to a significant level without subsequent drawing. The *d*-value of the (002) plane increased with increases of take-up velocity and draw ratio. On the other hand, the *d*-values of the (010) and (001) planes decreased. In all cases, the increased *D*-values were obtained, which was in good agreement with the tendency of birefringence. From the cold-drawn specimen, the kink band structure was revealed to confirm the microphase domains formed by the slip of plane, which disappeared in the zone-drawn specimen. The high draw ratio obtained at higher drawing temperature and drawing stress played an important role in marked increases of strength and modulus. In the near future, we will report on structure and properties of drawn PTT fibers spun at various solution concentrations.

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